

Title	The anomalous effect of high-intensity ultrasound on paper fibre-filler combinations
Type	Article
URL	http://ualresearchonline.arts.ac.uk/1939/
Date	2009
Citation	Manning, Andrew and Fricker, Anna and Thompson, Robert (2009) The anomalous effect of high-intensity ultrasound on paper fibre-filler combinations. Pigment & Resin Technology, 38 (4). pp. 218-229. ISSN 03699420
Creators	Manning, Andrew and Fricker, Anna and Thompson, Robert

Usage Guidelines

Please refer to usage guidelines at <http://ualresearchonline.arts.ac.uk/policies.html> or alternatively contact ualresearchonline@arts.ac.uk.

License: Creative Commons Attribution Non-commercial No Derivatives

Unless otherwise stated, copyright owned by the author

The anomalous effect of high intensity ultrasound on paper filler-fibre combinations

Anna Fricker, Andrew Manning & Robert Thompson

London College of Communication, MATAR Research Centre, University of the Arts London, London, UK.

Abstract

The purpose of this paper is to explore the previously unreported phenomenon in which changes occur to the particle size distributions of calcium carbonate fillers, used in papermaking, when exposed to high intensity ultrasound. Commercial paper pulps sonicated at a frequency of 20kHz are found to produce aggregates of their mineral filler constituents. The effects of sonication on isolated long and short fibre, and ground and precipitated calcium carbonate filler systems are also investigated both with and without the presence of dispersants. The findings are supported by particle size analysis and scanning electron microscopy of the sonicated systems.

It is clearly shown that exposure to high intensity ultrasound induces filler aggregation. However, the effect only occurs when paper fibres and fillers coexist and is not apparent for suspensions of filler only or fibre only slurries. Furthermore, the treatment overrides the effect of dispersants used to keep filler in suspension during the manufacturing process. An accompanying fall in pH with increasing sonication times is also noted and is linked to these changes. It is proposed that radical species produced in the slurries during sonication may explain the observed phenomenon. The role of pH is not clearly understood and needs further study.

The findings may be of interest in paper manufacture where uniform dispersal of fillers throughout the pulp is of significant importance. The phenomenon described in this paper has not previously been reported or explored. Further studies may add to knowledge of filler dispersions and their behaviour in papermaking.

Introduction

During the exploration of the effect of 20kHz high intensity ultrasound on the de-inking of HP Indigo printed papers (Fricker et al., 2006) we observed that prolonged exposure resulted in an increase in particle sizes centred on 22.7 microns (Figure 1).



Figure 1 Mean particle size distribution of the filtrates from Media Print paper printed with Indigo text and image and sonicated at 20°C

Filtrates of the de-inked paper were passed through a Beckman Coulter LS230 to establish the particle size ranges present. The Coulter plotted differential volumes of particles, representing frequency, against their size ranges. It was observed that for zero minutes of irradiation three main peaks were produced at 2.6, 22.7 and 70 microns. As the time of irradiation was increased through five, ten and twenty minutes the main peak at 22.7 microns increased successively in size at the expense of the two side peaks. However the reduction of peaks corresponding to larger particle sizes could be tentatively explained by disintegration of larger aggregates or flocs of particles. The shift of particle size volumes from the lower ranges to the higher values of the main peak suggested that aggregation of smaller particles to a common size range peaking at 22.7 microns was taking place. Similar effects were observed for all systems subsequently studied. However, the maximum peak value varied between about 22 to 33 microns for different systems, suggesting that the effect has less to do with the sonication frequency and more to do with the materials involved. Since ink particles had been removed by filtration it seemed likely that the particles now involved were probably those of the fillers and coatings used in the manufacture of the paper. This work identifies a phenomenon not previously reported in the literature and describes the systematic progression of experimental work undertaken to investigate it.

Fillers in the form of calcium carbonate are added to cellulose fibre papermaking slurries, primarily to fill the voids in the network of fibres which result from the papermaking process and increase the opacity of the final paper. Two forms of calcium carbonate may be used; ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). The particle sizes employed lie in the range 0.1 to 10 microns.

The surface of calcium carbonate is slightly cationic but carries only a small positive charge which is insufficient to provide adequate repulsion to prevent aggregation and coagulation of the filler particles. However, because calcium carbonate is slightly soluble in water, positively charged calcium ions are present in the aqueous phase and these adsorb onto the calcium carbonate surface, increasing repulsion. There is, however, still a tendency to aggregate and these pigment suspensions are stabilised using dispersants, usually polyacrylates. Polyacrylates are strongly anionic and create an electrical double layer around the pigment particles, resulting in their mutual repulsion (Sanders, 1991, Backfolk et al., 2002).

The stability of filler dispersions is pH dependent. The dissolution of free calcium ions from the solid calcium carbonate increases as the pH of the continuous phase is decreased; the concentration of free hydrated calcium ions in the equilibrium solution increases. The free calcium ions produced neutralise the negatively charged polyacrylate layer and reduce the efficiency of the double layer, destabilising the filler suspension (Greene and Rederd, 1974, Jarnstrom, 1993). The efficiency of the polyacrylate as a dispersing agent decreases as the amount of bound ions per polymer unit increases with decreasing pH.

The fibres used in papermaking are cellulosic. Cellulose becomes negatively charged when placed in water due to ionisation of the cellulosic hydroxyl groups (Gregory, 1993, Gama et al., 1997). The resulting charges on the surface of the cellulose fibres induce a redistribution of positively charged mobile calcium ions in the solution and an electrical double layer is produced. The mutual interaction of the electrical double layers of two approaching particles originate repulsive and attractive forces, Coulombic and Van der Waals respectively; these reduce the tendency to aggregate. The strength of this interaction may be influenced by the existence and effects of a hydration layer.

Commercial PCC is not necessarily treated with dispersant when supplied. In pure form, when dispersed at high concentrations in distilled water, it has a small positive charge. It therefore deposits on the negatively charged cellulose fibres. However, the positive charge on the particles is too weak for mutual repulsion. Thus non-dispersant systems aggregate to form unstable colloidal suspensions. At low concentrations PCC has a negative charge (Vanerek et al., 2000a, Vanerek et al., 2000b). Untreated GCC behaves similarly to PCC. Ground calcium carbonate and PCC are treated with dispersants such as polyacrylates.

Experimental – De-inking

The de-inking experiments were carried out on Indigo printed samples. These consisted of text and images printed on Media Print and Sapphire-coated papers. A solid inked image was also printed on both papers.

Pulps of 3% consistency were prepared by first tearing the samples into small squares, soaking them in distilled water overnight at room temperature, then pulping in a British Standard disintegrator for 3000 counts, also at room temperature. The disintegrated pulps were then diluted to a 1.5% consistency using distilled water at the intended sonication temperature. The stocks were sonicated for 0, 10 and 20 minutes.

The ultrasound equipment was supplied by FFR Ultrasonics Ltd, Leicester, UK, and consisted of a quartz piezoelectric transducer transferring vibrations at around 20kHz to a titanium alloy horn (AL2.5/3V). The electrical input into the ultrasound transducer was approximately 1.1kW giving a maximum power density of 188kWm^{-2} . The absolute ultrasound intensity was not known because no reliable commercial method for measuring cavitation energies is yet available (Thompson and Manning, 2005). The constancy of the electrical power input was monitored at 60-second intervals.

The pulps were maintained at $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$ during sonication by cooling the surround bath with dry ice in methanol. A mechanical stirrer was necessary to provide a uniform heat distribution and the temperature of the sample bath was monitored at 60-second intervals.

Following sonication the pulps were passed through a 50line/inch sieve and the filtrates collected for analysis.

Results and Discussion

Filtrates obtained from Indigo prints on Media Print paper showed a shift of particle size ranges from 2.6 and 70 microns to 22.7 microns. Experiments repeated at 20, 40 and 60°C showed the same trends (Figures 2a, 2b, 2c). The experiments were repeated for Indigo prints on Sapphire-coated paper, in order to establish whether the presence of paper coating influenced the result. The same trends were observed of the smaller peaks coalescing into a large single peak having a maximum differential volume in the range 22 to 33 microns (Figure 3).

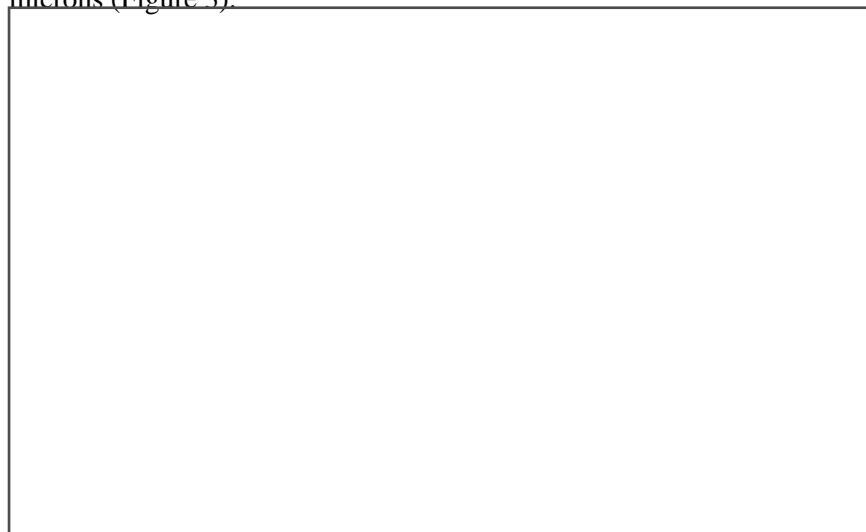


Figure 2a Mean particle size distribution of the filtrates from Media Print paper printed with Indigo text and image and sonicated at 20°C

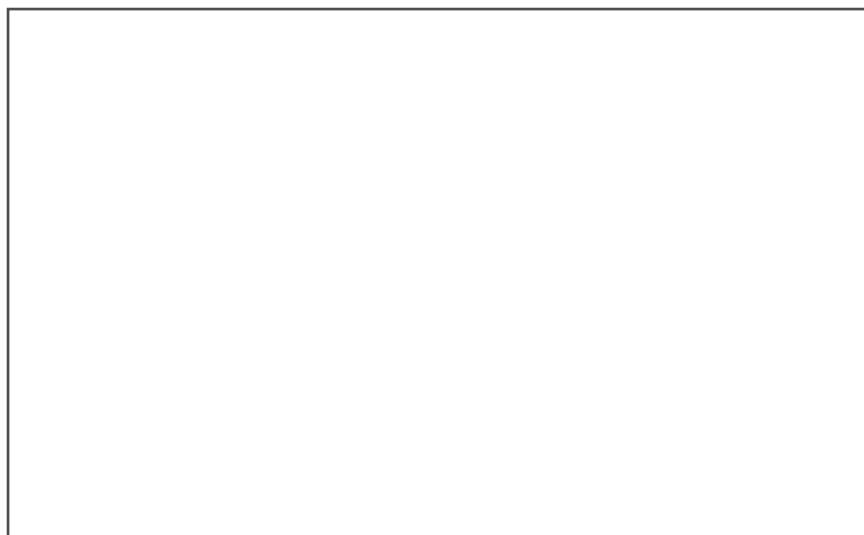


Figure 2b Mean particle size distribution of the filtrates from Media Print paper printed with Indigo text and image and sonicated at 40°C

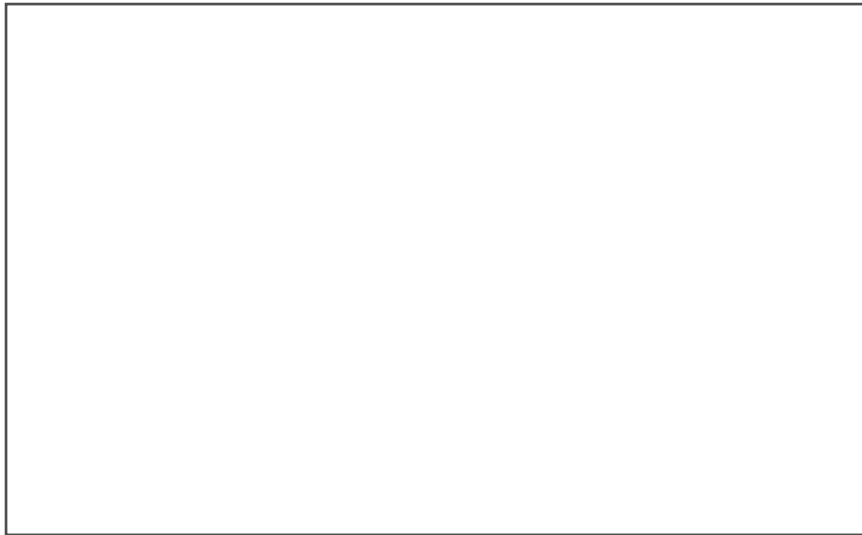


Figure 2c Mean particle size distribution of the filtrates from Media Print paper printed with Indigo text and image and sonicated at 60°C

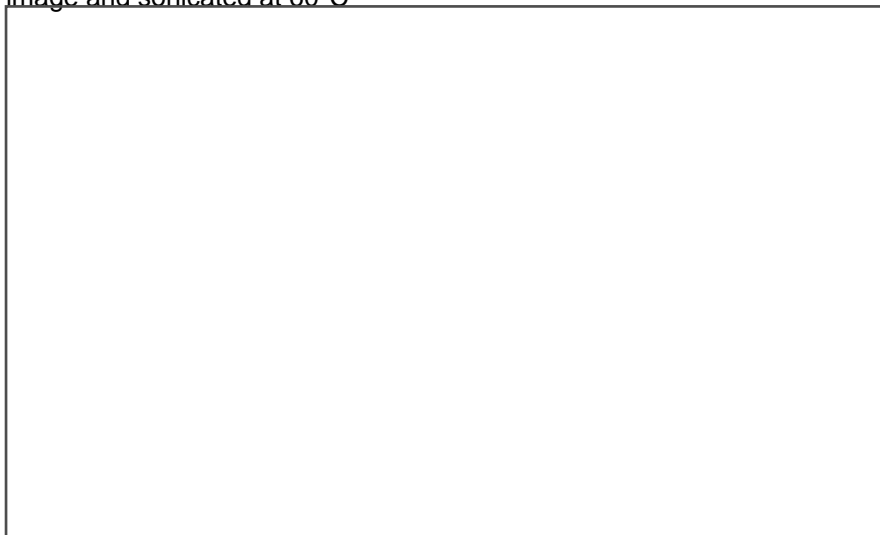


Figure 3 Mean particle size distribution of the filtrates from Sapphire-coated Media Print paper printed with Indigo text and image and sonicated at 20°C

In order to eliminate the possibility of ink particle interference, work was then concentrated on a range of unprinted papers. Papers examined included blotting paper, cartridge paper (Figure 4a), gloss art paper (Figure 4b), Lapponia pine virgin fibre, Media Print paper (Figure 4c) and Media Print paper treated with a Sapphire coating (Figure 4d). For these tests, the pulps were made at a 1.5% consistency and sonicated at a power input of approximately 1.0kW. Sonication was performed by dividing the stock into batches and sonicating each batch separately for 0, 10 and 20 minutes. The power input and temperature readings were recorded at 60-second intervals. The temperature was maintained at $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$. All filtrates showed the same profiles with the exception of the gloss art paper which produced a higher peak at 130 microns which reduced to a secondary peak at 48 microns alongside a smaller peak at 22.7 microns. This was possibly derived from breakdown of the paper coating. It seemed likely that the predominance of the peak at 22.7 microns was due to fillers used in the paper manufacture as the same was observed for coated and uncoated papers.

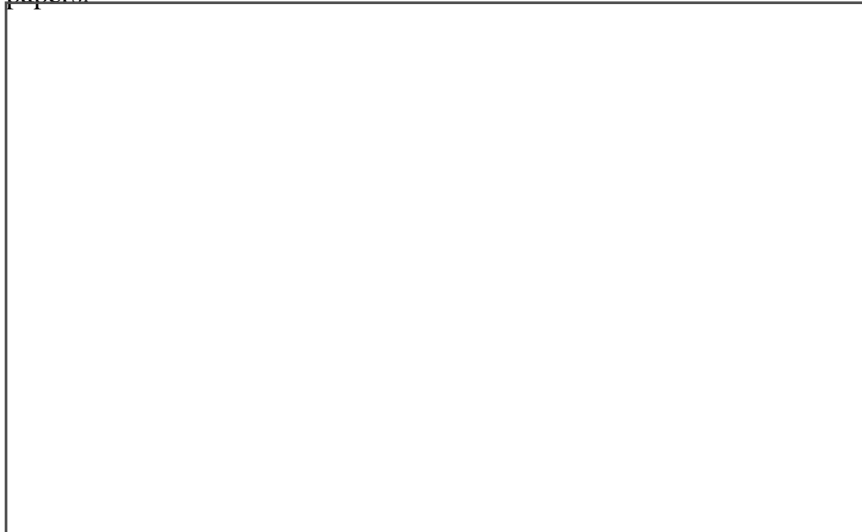


Figure 4a Mean particle size distribution of the filtrates from cartridge paper, sonicated at 20°C

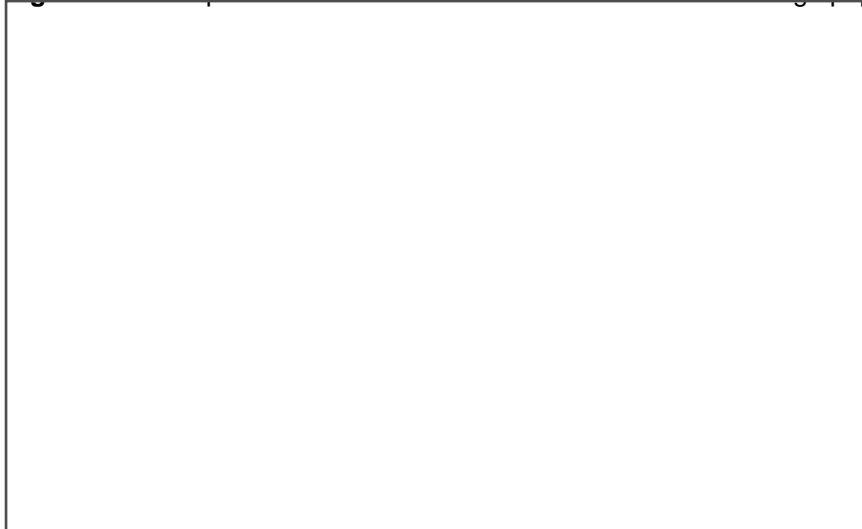


Figure 4b Mean particle size distribution of the filtrates from gloss art paper, sonicated at 20°C

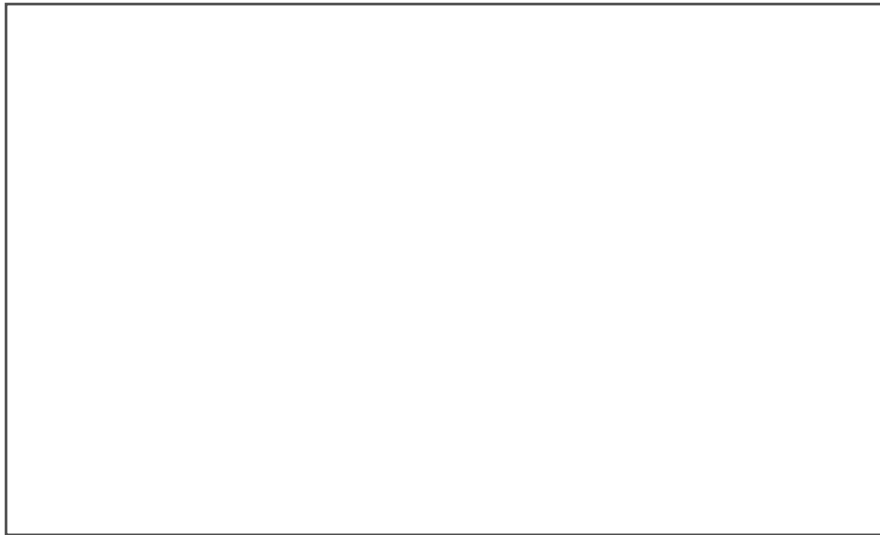


Figure 4c Mean particle size distribution of the filtrates from Media Print paper, sonicated at 20°C

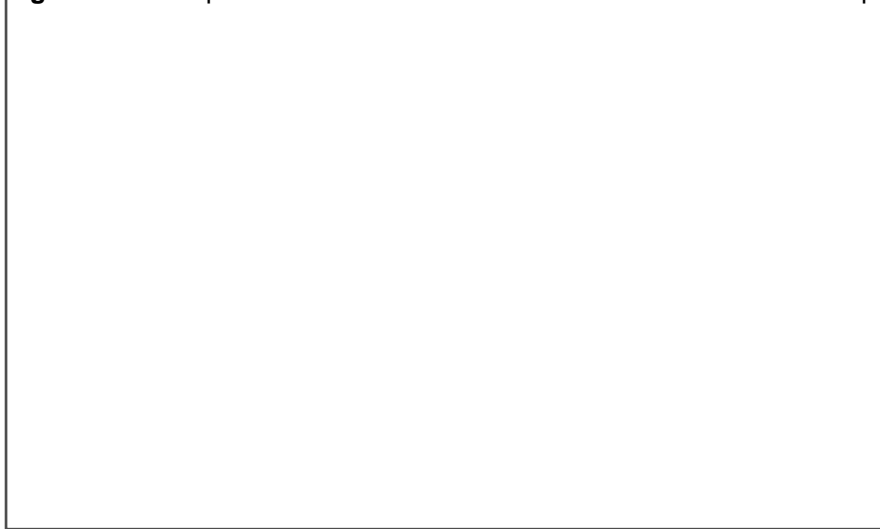


Figure 4d Mean particle size distribution of the filtrates from Sapphire-coated Media Print paper, sonicated at 20°C

Experimental - Consideration of Fibres and Fillers

To clarify the phenomenon, a series of experiments was devised to establish the relative role of fibres and fillers. High intensity ultrasound treatments were made on pure fibres containing no fillers. Two types of fibre were also selected for testing; samples of both long and short fibre were provided by M-Real (Sittingbourne).

High intensity ultrasound treatments were then made on pure fillers containing no fibres. The fillers selected were dispersed ground calcium carbonate (dGCC), dispersed precipitated calcium carbonate (dPCC) and undispersed precipitated calcium carbonate (uPCC). All fillers were supplied as pre-prepared slurries by Imerys Minerals Ltd (Sundsvall).

The initial pH was recorded and the stock was then sonicated in a stepwise process for a total period of 20 minutes using a 20kHz horn. At intervals of 1, 2, 5, 10 and 20 minutes, sonication was stopped and the pH of the stock was recorded. The pH of the stock was measured using a Hanna HI 9025pH meter with a Schott pH electrode, BlueLine 11pH, that had undergone a two point calibration before use. A 100ml sample of stock was removed at each interval for analysis and replaced with 100ml distilled water. The pH was measured again before sonication resumed.

All samples of short and long fibres without filler, showed dominant peaks in the range 22 to 33 microns with multiple lesser peaks at higher values (Figures 5a, 5b, 5c, 5d). Sonication for periods up to 20 minutes showed no significant changes in the relative positions or sizes of these peaks and it was concluded that ultrasound had no effect on the fibre size distribution.

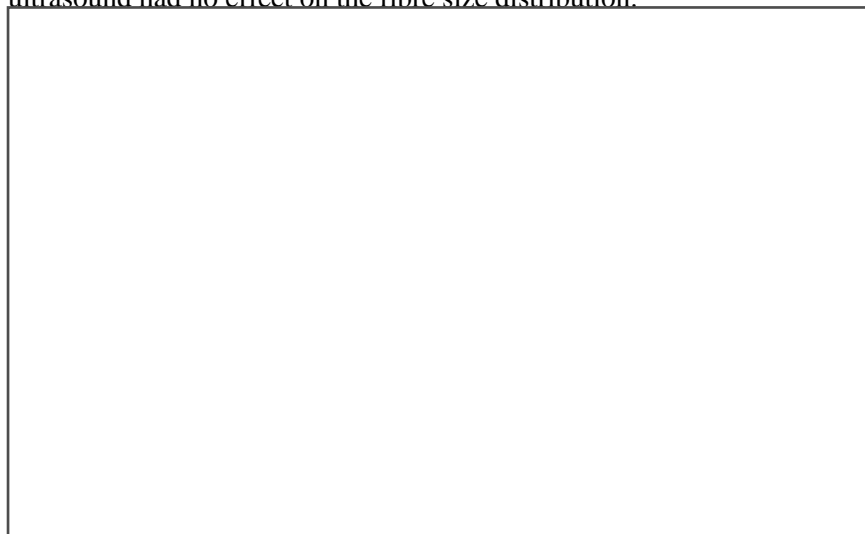


Figure 5a Mean particle size distribution of the filtrates from Lapponia pine virgin fibre, sonicated at 20°C



Figure 5b Mean particle size distribution of the filtrates from short fibre, sonicated at 20°C

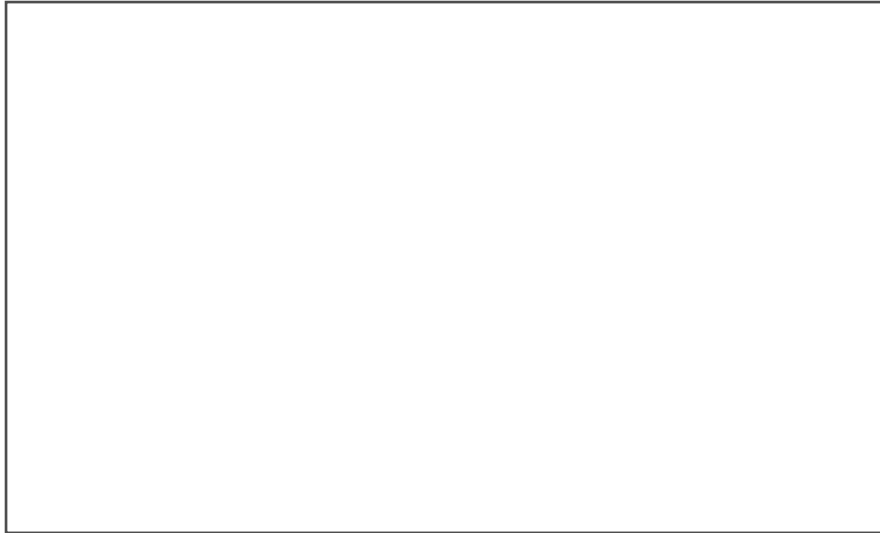


Figure 5c Mean particle size distribution of the filtrates from long fibre, sonicated at 20°C

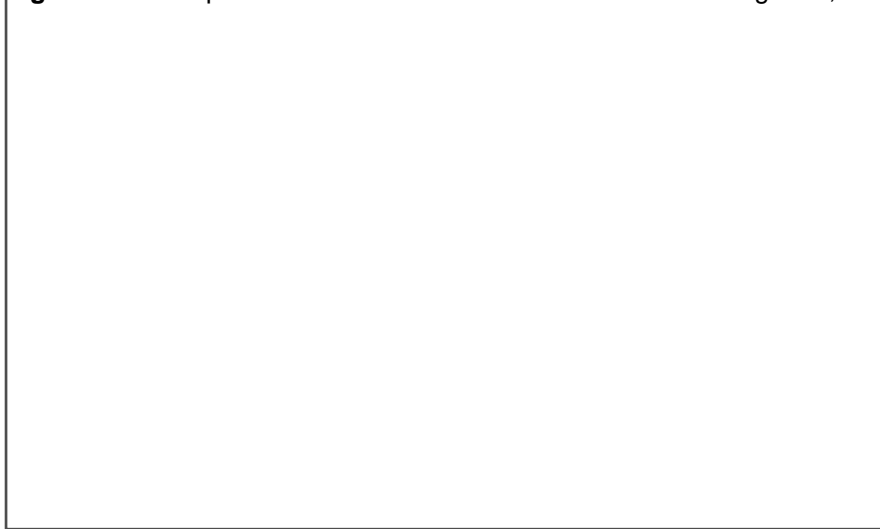


Figure 5d Mean particle size distribution of the filtrates from short fibre, sonicated at 20°C

Of the fillers, uPCC displayed a dominant peak at 5.1 microns with much smaller dominant peaks down to 0.1 microns giving a typical particle size of around 5 microns (Figures 6a, 6b). Ultrasound exposure times of up to 10 minutes showed little change in the profiles. Dispersed GCC was represented by a dominant peak at 1.7 microns with smaller peaks at around 20 microns, representing aggregates which broke down under ultrasound and reinforced the main peak (Figure 6c). Overall, the influence of ultrasound did not produce the 22 to 33 micron peak noted for papers containing fillers. It is evident then that fillers and fibres in isolation do not combine to produce particles in this size range.

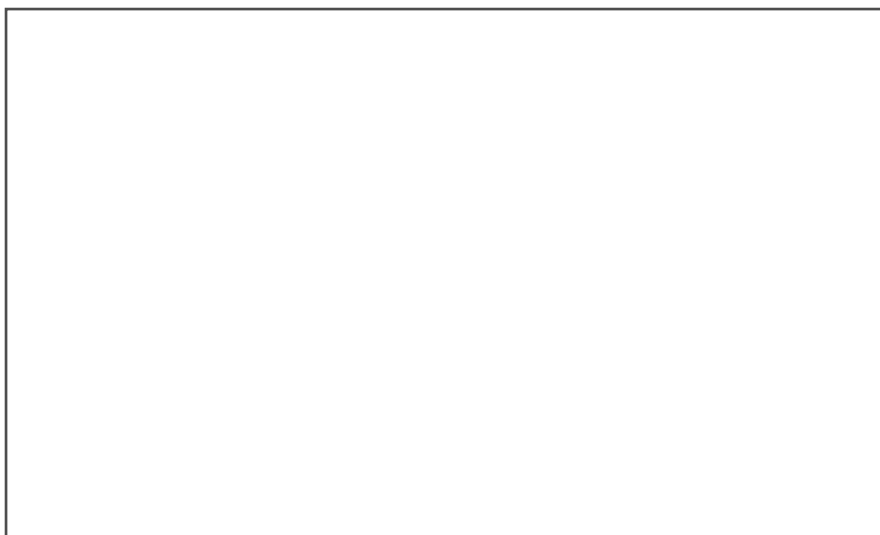


Figure 6a Mean particle size distribution of the uPCC filler, sonicated at 20°C



Figure 6b Mean particle size distribution of the uPCC filler, sonicated at 20°C



Figure 6c Mean particle size distribution of the dGCC filler, sonicated at 20°C

Fibre plus filler preparations

Having established that the enlargement of the 22 to 33 micron peak did not occur for either fillers or fibres sonicated separately, combinations of fibres and fillers were prepared and sonicated. A stock of virgin short fibre was prepared. The selected filler was then added to the pulped fibre to create a stock at 0.45% filler consistency (30% of fibre weight). The stock was agitated with a mechanical stirrer for 10 minutes to disperse the filler. All stocks were then sonicated under the same conditions described in the previous section.

For analysis, 10ml of each preparation was diluted by 50% to give a consistency of 0.75%, with 10ml distilled water at room temperature. The particle size distribution was determined using a Beckman Coulter LS230 particle size analyser with five separate runs being performed for each preparation.

Slides at a 0.4% and 0.1% consistency were also prepared for microscopic analysis by applying approximately a 1ml drop of each preparation to the slides and allowing them to evaporate. The same procedure was repeated for short fibre only pulp. Optical and scanning electron microscopy was used to examine the slides. Optical microscopy was performed with a Zeiss Axioskop 4.0 where the slides were examined under transmitted brightfield illumination. A Hitachi S-2600N scanning electron microscope was used in variable pressure mode also to inspect the slides. Images were captured using a backscattered electron detector.

Samples of short fibre plus uPCC and short fibre plus dPCC stocks were prepared and sonicated; also samples of long fibre plus filler stocks of the same consistency. Filtrate samples taken during sonication were analysed.

Long fibre plus uPCC filler showed a growth in the 22 to 33 micron peak at the expense of smaller particles at 3.5 microns and some loss of aggregates above 70 microns (Figure 7a); long fibre plus dPCC filler showed a similar trend (Figure 7b). Filtrates from short fibre slurries containing dPCC or uPCC behaved in the same way (Figures 7c, 7d). Filtrates from long fibre slurries plus dGCC showed a similar trend away from a dominant peak at around 1.7 microns to a less pronounced 22-33 micron peak (Figure 7e). However, filtrates from short fibre slurries containing dGCC filler showed a less pronounced trend (Figure 7f).

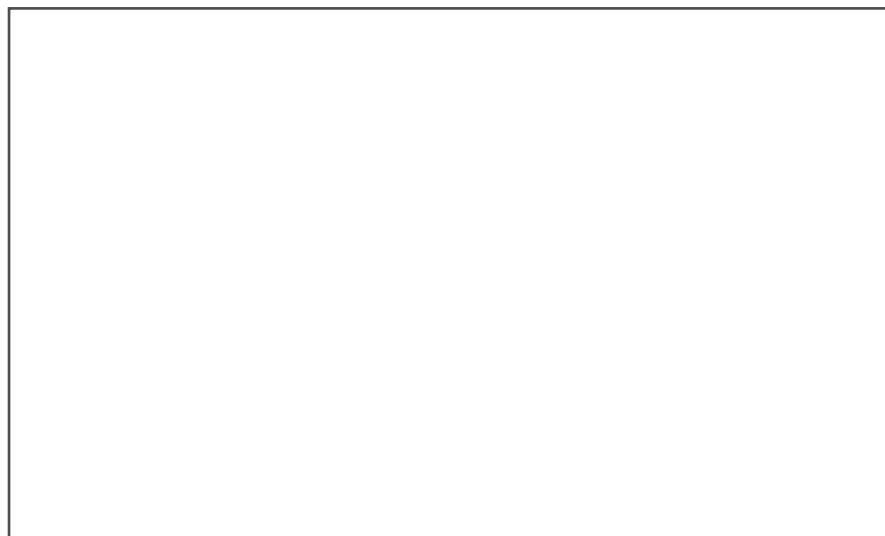


Figure 7a Mean particle size distribution of the filtrates from long fibre plus uPCC filler, sonicated at 20°C



Figure 7b Mean particle size distribution of the filtrates from long fibre plus dPCC filler, sonicated at 20°C

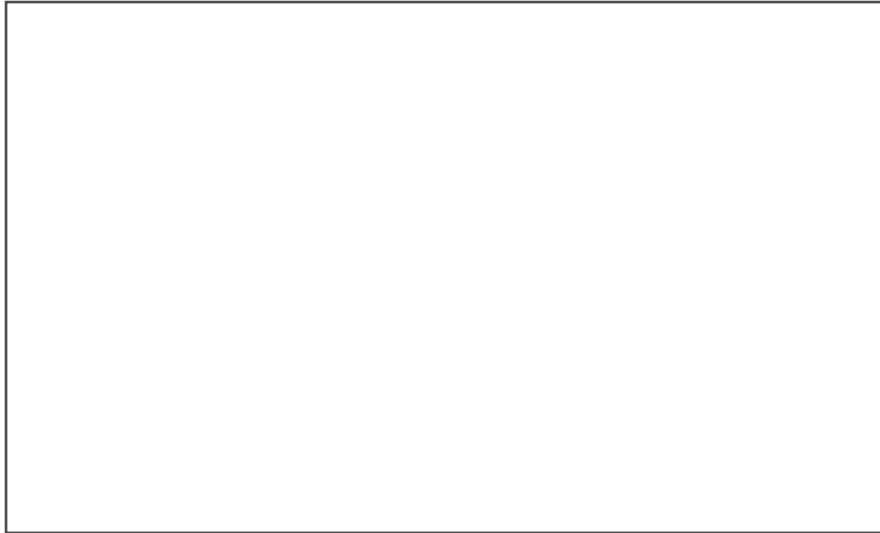


Figure 7c Mean particle size distribution of the filtrates from short fibre plus uPCC filler, sonicated at 20°C

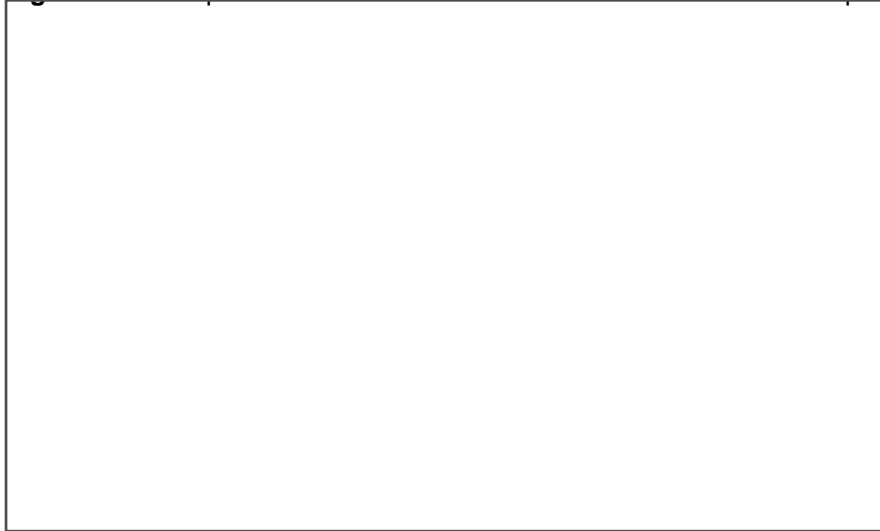


Figure 7d Mean particle size distribution of the filtrates from short fibre plus dPCC filler, sonicated at 20°C

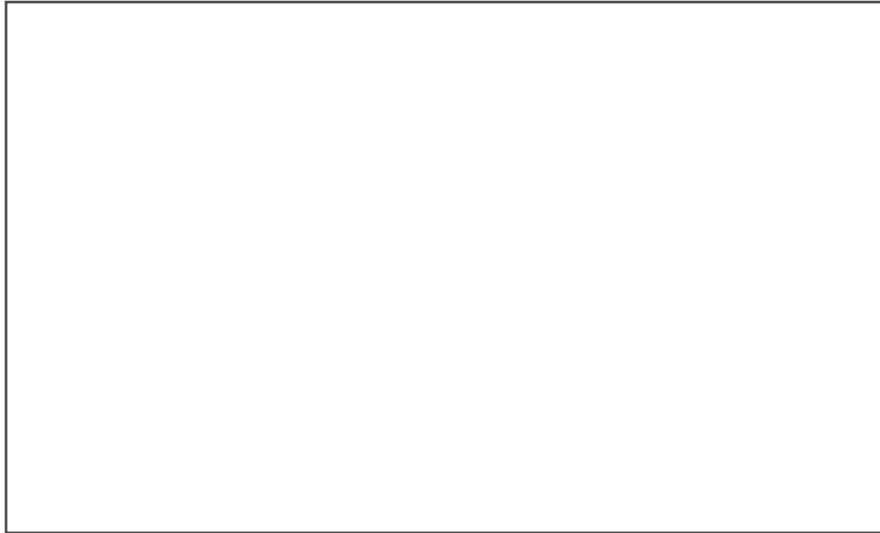


Figure 7e Mean particle size distribution of the filtrates from long fibre plus dGCC filler, sonicated at 20°C

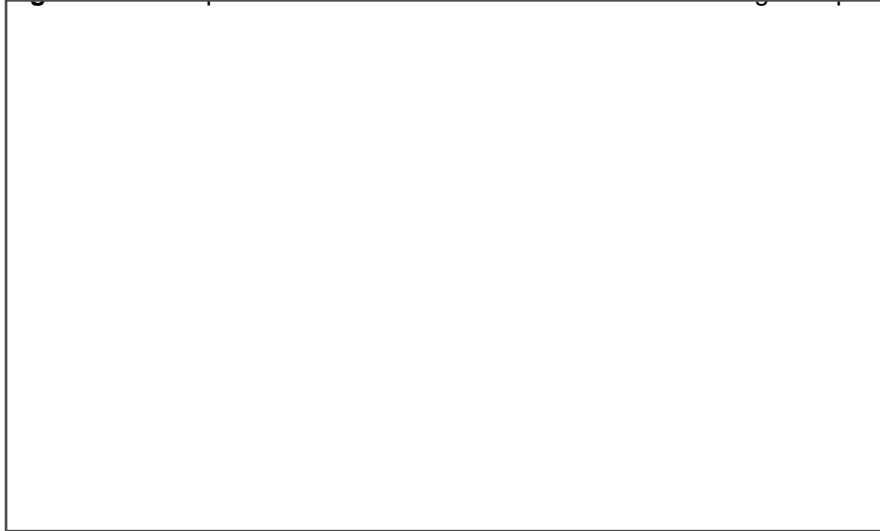


Figure 7f Mean particle size distribution of the filtrates from short fibre plus dGCC filler, sonicated at 20°C

Further analysis

A series of experiments was designed to explore whether the observed effects were present in the filtrate alone or whether they also existed in the unfiltered pulp. This was to establish whether the aggregation of filler/fibre occurred in: the bulk medium, in the more dilute filtrate environment or in both.

Pulp stocks were prepared in the usual way for short fibre only, short fibre plus uPCC, dPCC and dGCC filler. Samples were sonicated for 0, 1, 2, 5, 10 and 20 minutes and particle size distributions analysed using the Coulter. Filtrates were extracted in the usual way but in addition, samples of 'pulp stock' and 'filter residue' were also taken.

Three preparations were made from every stock. These were designated as 'stock', 'residue' and 'filtrate'. To obtain the filtrate, 50ml of stock was drained through a 50line/inch mesh sieve (approximately 500µm) and pressed. The residual fibre mat was then re-dispersed in 50ml distilled water and agitated to represent the residue. A further 50ml of stock was taken to provide the stock sample.

As with earlier work, both sonicated and unsonicated filtrates of short fibre alone showed no significant

changes in size distribution with the usual recurrent 22-33 micron peak (Figures 8a, 8b). On the other hand, the stock and residue samples showed two broad, distinct peaks at 200, and 600 microns in addition to the 22–33 micron peak (Figures 8c, 8d). The presence of the former two peaks is not surprising since the filtration mesh prevents the passage into the filtrate of particles and fibres much above 300 microns; sonication had no effect on any of these peaks.

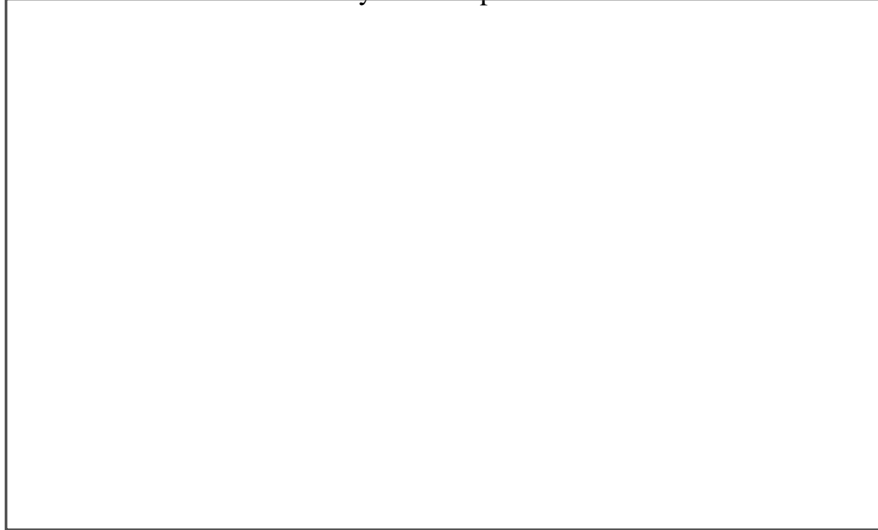


Figure 8a Mean particle size distribution of the filtrate from short fibre, unsonicated

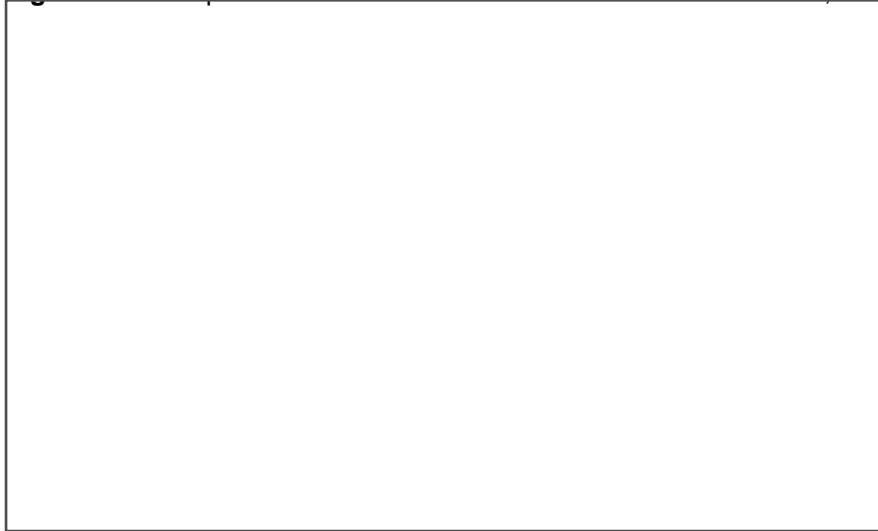


Figure 8b Mean particle size distribution of the filtrates from short fibre, sonicated at 20°C



Figure 8c Mean particle size distribution of the residues from short fibre, sonicated at 20°C



Figure 8d Mean particle size distribution of the stocks from short fibre, sonicated at 20°C

Filtrate samples of combined short fibre plus uPCC showed peaks at 0.2 and 4.0 microns found with dPCC filler, along with peaks at 23.0 microns and a smaller peak at 200 microns which may be due to fines passing through the mesh. The stock and residue samples gave the same three peaks as for short fibre only, plus the side peak at 6 microns found in the filtrate for PCC (Figures 9a, 9b, 9c). Sonication for 0, 1, 2, 5, 10 and 20 minutes produced a reduction in the 6 micron peak and a corresponding gain in the 23 micron peak, the two higher peaks being largely unaffected (Figures 10a, 10b, 10c).

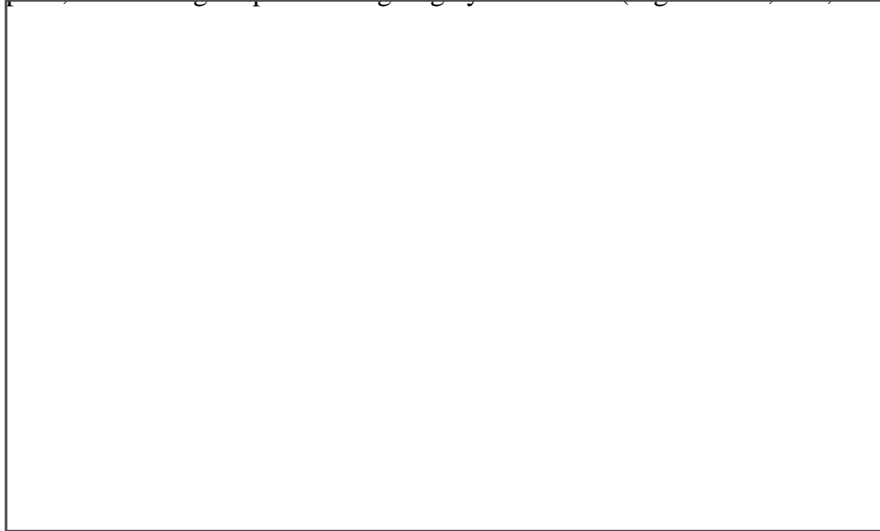


Figure 9a Mean particle size distribution of the filtrate from short fibre plus uPCC filler, sonicated at 20°C

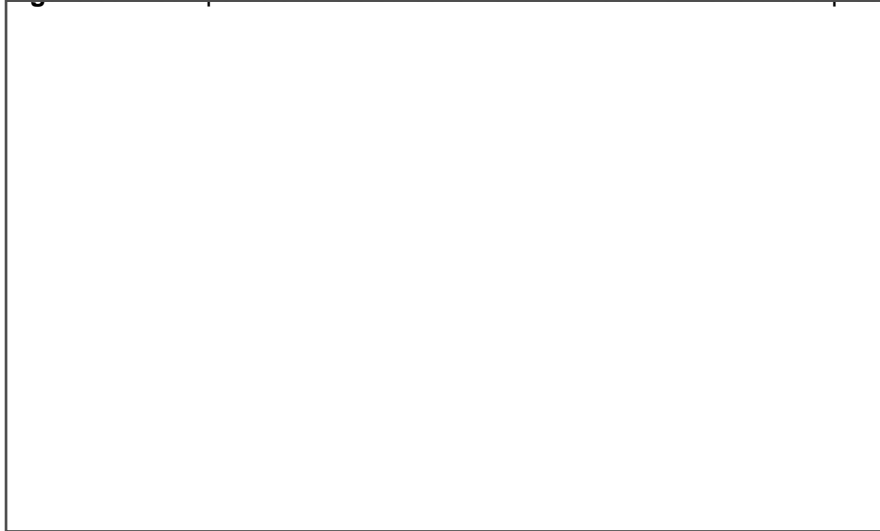


Figure 9b Mean particle size distribution of the residue from short fibre plus uPCC filler, sonicated at 20°C



Figure 9c Mean particle size distribution of the stock from short fibre plus uPCC filler, sonicated at 20°C



Figure 10a Mean particle size distribution of the filtrates from short fibre plus uPCC filler, sonicated at 20°C



Figure 10b Mean particle size distribution of the residues from short fibre plus uPCC filler, sonicated at 20°C

20°C

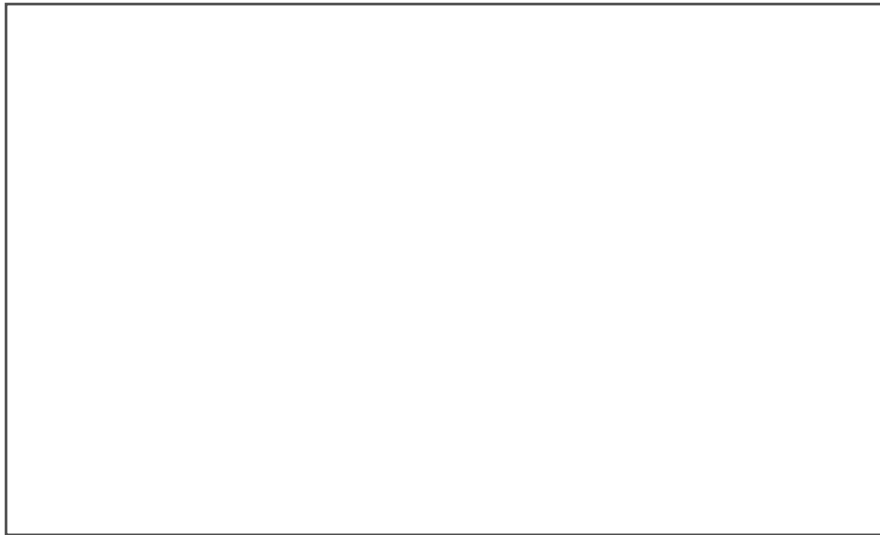


Figure 10c Mean particle size distribution of stocks from short fibre plus uPCC filler, sonicated at 20°C

Results for short fibre plus dGCC followed a similar pattern with the filtrate showing a large, broad peak spanning 0.2 to 10 microns, with a maximum at around 1.5 microns corresponding to dispersed filler and a smaller broad peak centred around 23 microns (Figure 11a).

The stock for these samples showed the same three peaks at 23, 200 and 600 microns as for the previous fibre only samples but with an additional side peak at around 4 to 6 microns corresponding to dGCC filler (Figure 11b). The residue obtained after expressing the pulp showed a large reduction in this side peak (Figure 11c) suggesting that filler had passed through the mesh and was now represented in the filtrate. The stability of all preparations was confirmed for periods of up to four days.

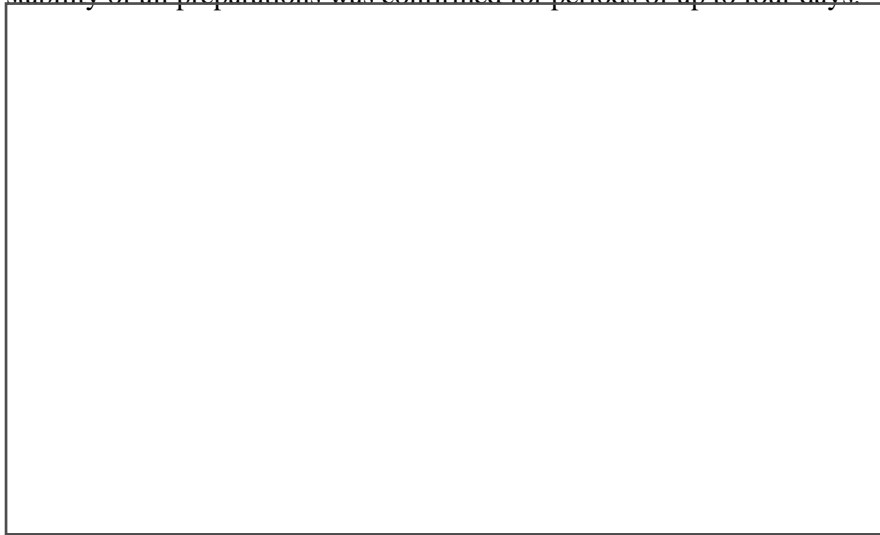


Figure 11a Mean particle size distribution of the filtrate from short fibre plus dGCC filler, sonicated at 20°C



Figure 11b Mean particle size distribution of the stock from short fibre plus dGCC filler, sonicated at 20°C

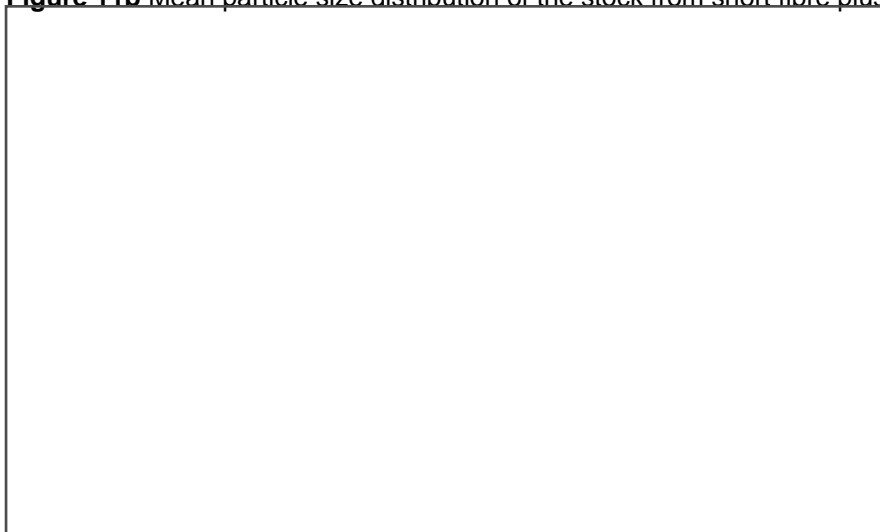


Figure 11c Mean particle size distribution of the residue from short fibre plus dGCC filler, sonicated at 20°C

The conclusions drawn from these studies were that aggregation effects were evident in the sonicated stock and residue as well as filtrate and were therefore independent of the filter mesh (Figures 12a, 12b, 12c, 12d). Aggregation must therefore occur prior to filtration.

The SEM images represented in Figures 12a to 12d show the progressive increase in filler populations accumulating in the presence of fibres as sonication times are increased.



Figure 12a Residue from the short fibre plus uPCC filler, unsonicated



Figure 12b Residue from the short fibre plus uPCC filler, sonicated for 1 minute at 20°C



Figure 12c Residue from the short fibre plus uPCC filler, sonicated for 5 minutes at 20°C



Figure 12d Residue from the short fibre plus uPCC filler, sonicated for 20 minutes at 20°C

The evidence suggests that ultrasound induced aggregation of the filler only takes place to any appreciable extent in the presence of cellulose fibres.

For this effect to appear in the filtrate, some fibre must pass through the mesh. Optical micrographs showed the presence of fibres or fines (Figure 13). Therefore, if fibre is involved in the aggregation process, fines which can pass through the mesh, rather than whole fibres must be present in the filtrates. Aggregates were found to form close to or on fibre fines in the filtrate (Figures 14a, 14b). There was also evidence of the possible contribution of fibrillation of fibres to the trapping of filler particles. Obviously fibres are present in the stock and residues; it is noted that growth in the 22 to 33 micron peak also occurs.

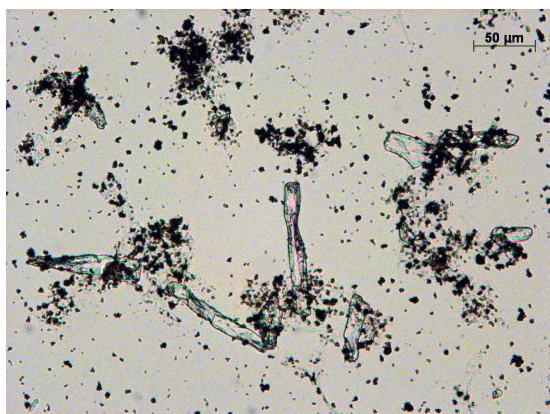


Figure 13 Filtrate from the short fibre plus uPCC filler, sonicated for 20 minutes at 20°C



Figure 14a Filtrate from the short fibre plus uPCC filler, sonicated for 1 minute at 20°C



Figure 14b Filtrate from the short fibre plus uPCC filler, sonicated for 10 minutes at 20°C

The role of pH

It had been noted that the pH of these slurries changed with irradiation time. Sonication changed the pH of many systems and may be an influencing factor on the formation of the peak common to 22 to 33 microns for mixed systems of filler and fibre. The effect of ultrasound was investigated for suspensions of fillers only, fibres only, long fibre plus fillers and short fibre plus fillers; distilled water and acidified water were run as controls. Sonication was carried out stepwise with pH readings being taken at intervals of 0, 1, 2, 5, 10, 15 and 20 minutes. The results are summarised in Table I.

The pH changes recorded below are for a total of ten minutes sonication.

System	pH Change	Decrease in pH
Distilled water	5.3 – 5.1	0.2
Acidified water	3.6 – 3.5	0.1
Fillers only		
dGCC	9.2 – 8.9	0.3
uPCC	8.2 – 6.9	1.3
Fibres only		
Short fibre	5.8 – 5.1	0.7
Long fibre	5.2 – 4.6	0.6
Fibre plus filler		
Long fibre plus dGCC	8.3 – 6.7	1.6
Long fibre plus uPCC	8.1 – 6.9	1.2
Long fibre plus dPCC	9.3 – 6.8	2.5
Short fibre plus dGCC	8.5 – 6.9	1.6
Short fibre plus uPCC	9.1 – 7.1	2.0
Short fibre plus dPCC	9.8 – 6.9	2.9

Table I Variation of pH with sonication

In order to determine whether the particle size distribution was affected by pH in the absence of sonication, further tests were performed on the long fibre plus dGCC filler stocks at room temperature. Stocks at a 1.5% fibre and 0.45% filler consistency were prepared as before. The pH of the stock was artificially lowered by the addition of dilute hydrochloric acid from pH 9.3 to 7.2 and samples of the stock were taken at regular intervals. These were then examined using the Coulter particle size analyser (Figure 15).

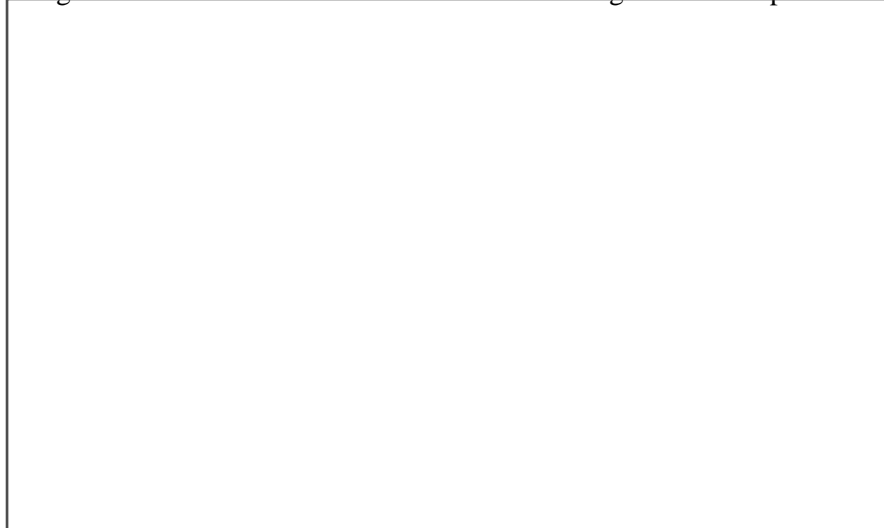


Figure 15 Mean particle size distribution of long fibre plus dGCC filler, pH varied

Tests were also performed on the fillers separately. These were dGCC from pH 9.0 to 7.6 and uPCC from pH 9.5 to 8.0. The filtrates were measured using the Coulter. No changes in particle size distributions were observed.

Results shown in Table I indicate that for fibres and fillers alone exposure to ultrasound produces only small pH changes and no aggregation (Figures 5 and 6). However combinations of fibres plus fillers give larger decreases in pH coupled with filler aggregation (Figures 7 and 14).

Importantly when the pH of fibre plus filler slurries was adjusted artificially no filler aggregation was observed. This clearly demonstrates that sonication plays a key role in the aggregation phenomenon.

Summary and Conclusions

A common feature of all the fibre-filler combinations is the presence of the peak located around 22-33 microns. The occurrence of this peak is independent of the application of ultrasound as it occurs for zero sonication but significantly increases in amplitude with successive doses of ultrasound. Changes in this peak do not occur for filtrates of fibre only or filler only suspensions and must therefore be a consequence of the co-existence of filler and fibre.

A number of active species are produced when water is exposed to high intensity ultrasound (Gray, 2008). These may include a complex mix of hydrogen and hydroxyl radicals, hydrogen and hydroxyl ions, hydrogen peroxide and superoxide radicals. The hydroxyl radical is a powerful oxidant with an oxidation potential (2.08V) which is greater than oxidising agents such as ozone (2.07V) and chlorine (1.39V) (Didenko and Suslick, 2002).

Changes in pH noted after sonication of distilled and acidified water were negligible because the active species quickly recombined in their dynamic state. Fibre in the presence of water, on the other hand, displayed a fourfold increase in the hydrogen ion concentration as reflected in the pH change, suggesting some interaction between fibre and the active species. Fibre and filler combinations gave much greater pH decreases suggesting a fifteen to eight hundred fold increase in the hydrogen ion concentration depending on whether the fillers were dispersed or undispersed. A correlation between increasing sonication and falling pH was found. All single systems of fibre or filler exhibited smaller pH changes than combinations of filler plus fibre.

In addition to the changes in particle size distributions noted above, SEM studies showed that filler congregated with or in the presence of fibres and fines and that the effect increased with increasing sonication times. Aggregation effects were evident in the sonicated stock and residue as well as their filtrates and were therefore independent of the filter mesh used to separate them.

The fibres used in papermaking are cellulosic. Cellulose becomes negatively charged when placed in water due to ionisation of the cellulosic hydroxyl groups. Calcium carbonate is slightly cationic because some calcium ions are present in the aqueous phase due to its slight solubility; these are adsorbed onto the surfaces of the mineral particles. Because of the slight cationic nature of the calcium carbonate and the anionic character imparted to the cellulose molecule by its hydroxyl groups, there is a slight tendency for the filler particles to be attracted to the cellulose fibres.

It is suggested that the hydroxyl radicals created during sonication oxidise sites on the calcium carbonate particles to form further surface calcium ions. With increasing sonication, the concentration of hydroxyl radicals increases creating further positive charges on the filler particles. Thus the attraction of the charged filler particles to the cellulose fibres is increased and the filler particles congregate progressively in the presence of fibres.

The decrease in pH with sonication is not fully understood at this stage and whether the change and the associated aggregation of filler/fibre species is incidental or instrumental is not clear and requires further exploration. However it has already been noted that lowering the pH has no effect on filler and filler plus fibre particle size distributions.

In the case of the dPCC filler, the polyacrylate polymers commonly used as dispersants are anionic and impart a negative charge to the filler. The pH influences the stability of the calcium carbonate slurry

because it is slightly soluble. Dissolution of calcium ions from the calcium carbonate increases as the pH decreases. This will happen with increasing sonication. Free calcium ions affect the efficiency of the electrical double layer and the stability of the calcium carbonate in suspension decreases as the pH decreases because the free calcium ions in solution neutralise the anionic polyacrylate. Hence the lower the pH, the lower the efficiency of the polyacrylate as a dispersant. This effect is evidenced in Figures 16a, 16b and 7a, 7b.

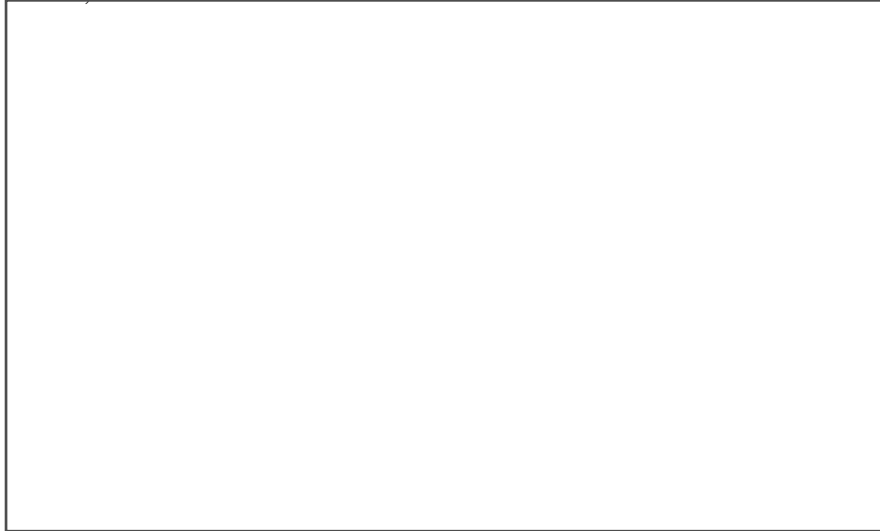


Figure 16a Mean particle size distribution of the filtrates from short fibre plus uPCC filler, sonicated at 20°C

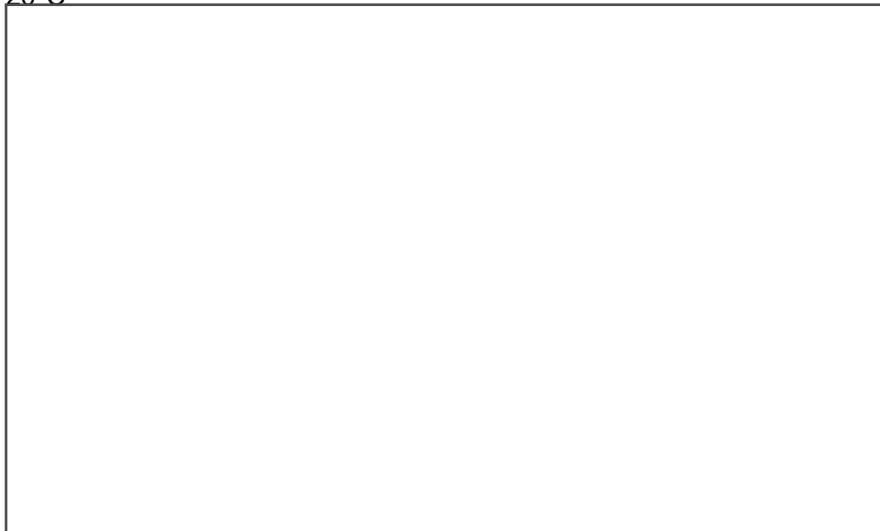


Figure 16b Mean particle size distribution of the filtrates from short fibre plus dPCC filler, sonicated at 20°C

The different rates of increase for these peaks may be explained as follows. The uPCC has a small, inherent positive charge which may be increased due to oxidation by the hydroxyl radicals produced by the ultrasound. On the other hand the dPCC has a net negative charge imparted by the adsorbed polyacrylate. The hydroxyl radicals may oxidise the surface of the calcium carbonate in the same way as for the undispersed material but because the negative charges on its surface have to be neutralised before it can take on a positive characteristic, the aggregation process which is immediately evident in the uPCC occurs much more slowly for the dispersed medium. Figures 16a, 16b, 7a, 7b clearly illustrate this. The smaller particles (in the presence of fibres) aggregate more slowly for the dPCC and the shift of peaks from below 10 to the 22-33 micron range is more gradual than for the same fibre containing uPCC. The effect is even more pronounced for dGCC plus fibre (Figures 17, 7e). Filler only systems remain fully dispersed after sonication due to the positive charges imparted and this may be seen in the SEM images for pure fillers.



Figure 17 Mean particle size distribution of the filtrates from short fibre plus dGCC filler, sonicated at 20°C

References

- Backfolk K., Lagerge S., Rosenholm J., Eklund D. (2002), 'Aspects of the interaction between sodium carboxymethylcellulose and calcium carbonate and the relationship to specific site adsorption', *J Colloid and Interface Science*, Vol 248, pp. 5-12.
- Didenko Y.T and Suslick K.S. (2002), 'The energy efficiency of formation of photons, radicals and ions during single bubble cavitation', *Letters to Nature, Nature*, vol. 418, 25 July.
- Fricker A., Manning A., Thompson R. (2006), 'Deinking of Indigo prints using high-intensity ultrasound', *Surface Coatings International*, vol. 89, B2, pp. 145-156.
- Gama F.M, Carvalto M.G, Figueiredo M.M, and Mota, M. (1997), 'Comparative study of cellulose fragmentation by enzymes and ultrasound', *Enzyme Microbiology Technology*, Vol. 20, pp.12-17.
- Gray Laboratory annual report. 'Free Radicals: nature's way of saying no or molecular murder', <http://www.graylab.ac.uk/lab/reviews/pwrev.html> Accessed 19/06/08.
- Greene B.W., Reder A.S. (1974), 'Electrokinetic and rheological properties of calcium carbonate dispersions used in paper coatings', *Tappi Journal*, Vol. 57, no. 5, pp. 101-106.

Gregory J. (1993), 'The role of colloidal interactions in solid-liquid separation', *Water Science*, Vol. 27, pp. 1-17.

Jarnstrom L.(1993), 'The polyacrylate demand in suspensions containing ground calcium carbonate', *Nordic Pulp and Paper Research Journal*, Vol. 8, no. 1, pp. 27-33.

Sanders N.D. (1991), 'The effect of surface modification of pigments on colloidal stability and structural performance', *Proceedings of the Symposium on Papercoating Fundamentals*, Montreal, pp. 51-60.

Thompson R., Manning A. (2005), 'A Review of Ultrasound and its Applications in Papermaking', *Progress in Paper Recycling*, Vol. 14, no. 2, pp. 26-42.

Vanerek A., Alince B., Van de Ven T.G.M. (2000), 'Colloidal behaviour of ground and precipitated calcium carbonate fillers: effects of cationic polyelectrolytes and water quality', *J. Pulp and Paper Science*, Vol. 26, no. 4, pp. 135-139.

Vanerek A., Alince B., Van de Ven T.G.M. (2000), 'Interaction of calcium carbonate fillers with pulp fibres: effect of surface charge and cationic polyelectrolytes' *J. Pulp and Paper Science*, Vol. 26, no. 9, pp. 417-322.